

### AMENDMENTS TO SPECIFICATION

**Please replace the paragraph beginning at page 3, line 21 as follows:**

Another approach is to employ ~~gasses~~ gases that permeate rubber more slowly than air. Two such gases are nitrogen and sulfur hexafluoride. However, each of these is expensive and cumbersome to employ. In the case of sulfur ~~hexafluoride~~ hexafluoride, internal pressure actually increases with time due to pneumatic pumping of air molecules from the outside the ball into the inside of the ball driven by the partial pressure gradient and limited by the relatively slow permeability of the sulfur hexafluoride. (Described in US 4,340,626).

**Please amend the paragraph beginning at page 4, line 13 as follows:**

An aspect of the present invention provides novel formulations for hollow or inflatable rubber articles, such as tennis balls, ~~basket-balls~~ basketballs, volleyballs, soccer balls, inner tubes, and tires having substantially improved barrier properties.

**Please amend the paragraph beginning at page 4, line 17 as follows:**

An aspect of the present invention provides novel millable polyurethane (MPU) ~~MPU~~/rubber alloys that provide enhanced barrier properties along with good balance of other mechanical properties, such as resiliency, strength etc.

**Please amend the paragraph beginning at page 4, line 26 as follows:**

An aspect of the present invention provides a composition of matter having a permeability to oxygen not greater than about  ~~$5.5 \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{seconds} \cdot \text{Pascal}$~~   $10^{-13}$   $(5.5 \text{ cm}^3 \text{ cm} / \text{cm}^2 \cdot \text{s} \cdot \text{Pa})$   $10^{-13}$  at 25°C.

**Please amend the paragraph beginning at page 5, line 9 as follows:**

Furthermore, alloys of this novel formulation exhibit an inflection point, in curves of oxygen permeability as a function of fractional MPU composition, at about 40% 40 wt% millable Polyurethane / 60% 60 wt% natural or synthetic ~~rubber~~ rubber.

**Please amend the paragraph beginning at page 5, line 13 as follows:**

A better understanding of further aspects, advantages, features, properties, and relationships of the invention will be obtained with the additional ~~detail~~ detailed description and examples appended below.

**Please amend the paragraph beginning at page 6, line 8 as follows:**

Polyisocyanates (2) may be aliphatic, cycloaliphatic, or aromatic such as hexanediiisocyanate, isophorone diisocyanate, cyclohexane diisocyanate, diphenylmethane diisocyanate, ~~ethylene~~ phenylene diisocyanate, naphthalene diisocyanate, as well as tri or higher isocyanates, containing two or more reactive isocyanate groups per molecule.

**Please amend the paragraph beginning at page 7, line 1 as follows:**

Polyurethanes can behave as elastomers or as rigid, hard thermosets. The stiffness and rigidity of the polymer typically increases as the relative percentage of hard block units increases. Further, as the symmetry and linearity of the hard block units increases, there is an increasing tendency of these units to form domains separate from the soft blocks. Hard block domains are characterized by strong intermolecular attractions and are referred to as crystalline

since heat is necessary to disrupt them. Hard block domains melt and disassociate over defined temperature ranges and they are characterized using techniques such as differential scanning calorimetry (DSC). As a sample is heated through a melting transition, a peak is observed in the heat flow curve. The size of this peak is proportional to the crystalline content of the sample. A substantial absence of a peak can be taken as an indication that the polyurethane is amorphous, that only a minimal amount, less than about 5 wt% ~~5%~~ crystallinity is present.

**Please amend the paragraph beginning at page 7, line 16 as follows:**

The term "substantially amorphous polyurethane" comprehends a polyurethane having less than about 5 wt% crystallinity ~~5% crystallinity~~ as determined by DSC or similar technique. Moreover, the term comprehends a polyurethane synthesized using essentially no polar or symmetrical chain extenders (3).

**Please amend the paragraph beginning at page 7, line 20 as follows:**

The term "millable polyurethane" ( MPU ) comprehends polyurethane materials that can be processed in conventional rubber equipment (often referred to as "milling") and MPU may be either amorphous or may have some crystallinity in the range of about 0-5 wt%, ~~0-5%~~, as determined by DSC or by an equivalent technique.

**Please amend the paragraph beginning at page 8, line 6 as follows:**

In order to limit the molecular weight and reduce the viscosity of the final MPU sufficiently to make the gum processable on conventional rubber processing equipment, the ratio

of polyol plus short chain glycol to polyisocyanate is greater than 1 (i.e.,  $[(1) + (3)] / (2) > 1$ ). Such monomer ratios result in the formation of little or no symmetrical hardblock in the finished MPU. The elastomer so formed is essentially, or substantially, amorphous. The MPU contains less than about 5 wt% 5% crystallinity as evidenced by the substantial absence of hard segment melting transitions in a DSC spectrum.

**Please amend the paragraph beginning at page 8, line 23 as follows:**

The diisocyanate (2) precursor of the MPU of the present invention is preferably, but not limited to, diphenylmethane diisocyanate and toluene diisocyanate. Suitable diisocyanates include, but are not limited to hexanediisocyanate, trimethylhexanediisocyanate, isophorone ~~isopherone~~ diisocyanate, cyclohexane diisocyanate, biscyclohexylmethane diisocyanate, norbornane diisocyanate, tetramethylxylene diisocyanate, tolylene diisocyanate, phenylene diisocyanate, naphthylene diisocyanate, and xylene diisocyanate ~~an dxylylene diisocyanate~~.

**Please amend the paragraph beginning at page 9, line 1 as follows:**

The short chain functional diol (chain-extender 3) precursor of the MPU of the present invention is preferably ~~preferabl~~, but not limited to, glycerol monoallylether and trimethylpropane monoallyl ether. Suitable short-chain diols include, but are not limited to diethylene glycol, tripropylene glycol, and 1,3 butanediol. However, polar chain-extenders, which tend to introduce hard segments, are essentially omitted from the synthesis.

**Please amend the paragraph beginning at page 9, line 7 as follows:**

The inventive formulation comprises substantially amorphous MPU because of the unexpected observation that barrier articles, such as air inflatable sports balls or tubes, manifest at least 2-3-fold better air retention as well as other desirable mechanical properties where produced from improved rubber formulations containing at least 10-40 wt% ~~10-40%~~ MPU alloyed with rubber. Moreover, polyurethanes containing substantial crystallinity are not mill processable and have higher air permeability. Furthermore, the inventive formulations, using MPU meet long-felt unmet needs of the sports balls industry.

**Please amend the paragraph beginning at page 10, line 6 as follows:**

MPU and rubber are mixed in the desired proportions in a banbury, or other suitable industry standard mixer. The mixture is masticated to obtain a good uniform blend and then is calendered or processed by some other industry standard mixing technique. Desired curatives, additives, and fillers are blended during ~~calendering~~ calendering. The various ingredients are mixed at a temperature that is low enough to prevent curing of rubber. The mixture is calendered for a time sufficient to obtain consistency suitable for use by subsequent molding machines

**Please amend the paragraph beginning at page 10, line 18 as follows:**

The term "balance of properties," comprehends material properties such as strength, modulus, elongation, hardness, resilience, and glass transition ~~temperature~~ a temperature that

affect the playability and performance of a sports ball, *e.g.*, tennis balls meet the USTA specifications with respect to deflection, rebound, air pressure, weight, and size.

**Please amend the paragraph beginning at page 10, line 23 as follows:**

Oxygen permeability was measured according to ASTM D1434 and a specification less than ~~5.0 cm<sup>3</sup>-cm/cm<sup>2</sup>-seconds-Pascal~~  $\times 10^{-13}$  (5.0 cm<sup>3</sup> cm/cm<sup>2</sup> · s · Pa) 10<sup>-13</sup> was established based on the benchmark established by the measurement of state of the art tennis ball cores as measured in GP-1, GP-2, and GP-4 in examples A, C, and E.

**Please amend the paragraph beginning at page 10, line 28 as follows:**

Barrier articles such as tennis balls, other air inflatable sports balls, tubes, and tires, are made by forming the inventive alloy into a desired shape using any of the several techniques suitable for forming rubber articles such as compression molding, transfer molding, ~~calendering~~ calendering, etc. Barrier articles are formed by curing the inventive MPU/rubber alloys in conventional molding equipment. The subsequent conventional downstream processing, necessary to form tennis balls, such as wrapping the rubber balls with felt, cutting the excess material, polishing, packing etc. before shipping cartons of tennis balls to customers or pro-shops is taught in US6030304; US5225258; and US5558325.

**Please amend the paragraph beginning at page 11, line 8 as follows:**

Polyester-based amorphous polyurethanes reduced gas permeability and temperature dependence more so ~~merese~~ than did PTMEG-based materials. However, polyester-based

materials did not facilitate the balance of properties suitable for tennis balls. Similar results may be expected for polypropylene ether-based amorphous polyurethanes. Consequently, the PTMEG-based MPU provides a coordinated benefit and is preferable for use in this invention. However, polybutadiene can be added to the alloy, which mitigates some of the deficiencies found in MPUs based on polyester or polypropylene ether glycol.

**Please amend the paragraph beginning at page 12, line 13 as follows:**

Alloys were formed by mixing either Adiprene<sup>®</sup> CM (ACM), Millathane<sup>®</sup> E-34 (ME34), or Millathane<sup>®</sup> M76 (MM76) with natural rubber components designated GP2 or GP4 in proportions indicated in the tables below. The MPU compositions included about 50% 50 wt% clay and other additives. As previously noted, GP2 and GP4 rubbers likewise included about 50% 50 wt% clay and other additives. The results of permeability testing is presented in the table below. Example alloys were made by milling together the natural rubber formulations with either ACM, ME34, or MM76 formulations. The various alloys were cured and tested for permeability. Table 1 below presents the properties of the cured samples. Table 2 presents permeability values and test conditions. Permeability results for conventional rubber formulations are provided as comparative examples. The data show that the novel alloys have improved gas retention with acceptably high resilience and strength. These data were taken in the presence of alloys comprising 50 weight% each of MPU and rubber. However, the ratio of MPU to rubber may be varied to suit specific applications.

Please amend Table 2 beginning on page 14 so that the units for "Est. Oxygen Permeability" now read as follows:

Table 2							
Example		Nominal Sample Thickness	Relative Humidity	Temp.	Pressure Gradient	Oxygen Trans. Rate	Est. Oxygen Permeability
	Description	Mils	%	deg. C	mm Hg	(21% O <sub>2</sub> ) cc/m <sup>2</sup> day	$\frac{\text{cm}^3 \text{ cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{Pa}} 10^{-13}$ $\frac{\text{Cc-cm}}{\text{cm}^2 \cdot \text{sec-Pa}} 10^{-13}$
1.	50/50 ACM/GP2	40	35	25	760	52	3.0
2.	50/50 ACM/GP2	40	35	37	760	95	5.4
3.	50/50ACM/GP4	42	35	25	760	80	3.4
4.	50/50ACM/GP4	42	35	37	760	104	6.2
A	GP2	38	35	25	760	98	5.1
B	GP2	38	35	37	760	174	9.3
C	GP4	43	35	25	760	95	5.8
D	GP4	43	35	37	760	183	10.0
5	50/50 ME34/GP2	40	35	25	760	81	4.6
6.	50/50 ME34/GP2	40	35	37	760	136	7.8
7.	50/50 ME34/GP4	40	35	25	760	85	4.8
8	50/50 ME34/GP4	40	35	37	760	85	8.2
9	50/50 MM76/GP2	35	35	25	760	31	1.6
10	50/50 MM76/GP2	35	35	37	760	64	3.2
11	50/50 MM76/GP4	31	35	25	760	46	2.0
12	50/50 MM76/GP4	31	35	37	760	90	4.0



**Please amend the paragraph beginning at page 15, line 1 as follows:**

Alloys of MPU and GP1, a natural rubber formulation including about ~~50%~~ 50 wt% clay and other additives, gave improved permeability relative to controls GP2 and GP4 and showed a strong correlation of temperature and permeability. The materials were prepared as in Examples 1-12, but tested as sheets examples. Example E is a sheet example was made from GP1.

Please amend Table 3 beginning on page 15 so that the units for "Est. Oxygen Permeability" now read as follows:

Table 3								
Example		290F Min Time	Nominal Sample Thickness	Relative Humidity	Temp.	Pressure Gradient	Oxygen Trans. Rate	Est. Oxygen Permeability
	Units	min	mils	%	deg. C	mm Hg	(21% O <sub>2</sub> ) cc/m <sup>2</sup> day	$\frac{\text{cm}^3 \text{ cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{Pa}} 10^{-13}$ $\frac{\text{cc-cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{Pa}} 10^{-13}$
13.	20/80 ACM/GP1	10	34	35	25	760	106	5.1
14.	40/60 ACM/GP1	10	32	35	25	760	77	3.5
15.	60/40 ACM/GP1	10	43	35	25	760	40	2.5
16.	80/20 ACM/GP1	15	34	35	25	760	35	1.7
17.	80/20 ACM/GP1	15	27	35	25	760	51	2.0
20.	80/20 ME34/GP1	15	27	35	25	760	92	3.5
21.	20/80 ME34/GP1	10	33	35	25	760	115	5.5
22.	40/60 ME34/GP1	10	34	35	25	760	87	4.2
23.	60/40 ME34/GP1	10	42	35	25	760	64	3.8
24.	80/20 ME34/GP1	15	32	35	25	760	59	2.7
E	GP1	10	24	35	25	760	256	8.7

Please amend Table 4 beginning on page 16 so that the units for "Est. Oxygen Permeability" now read as follows:

Table 4							
Example		Nominal Sample Thickness	Relative Humidity	Temp.	Pressure Gradient	Oxygen Trans. Rate	Est. Oxygen Permeability
	Description	Mils	%	deg. C	mm Hg	(21% O <sub>2</sub> ) cc/m <sup>2</sup> day	$\frac{\text{cm}^3 \text{ cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{Pa}} 10^{-18}$ $\frac{\text{Gs cm}}{\text{cm}^2 \cdot \text{sec} \cdot \text{Pa}} 10^{-10}$
25.	40/60 ACM/GP1	139	35	25	760	0.0633	2.7
26.	40/60 ME34/GP1	144	35	25	760	0.1194	5.2